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PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 2 : B63B 59/00; B08B 17/00; C09D 5/16; C08L 83/00	A1	(11) International Publication Number: WO 80/00554 (43) International Publication Date: 3 April 1980 (03.04.80)

(21) International Application Number: PCT/GB79/00146

(22) International Filing Date: 3 September 1979 (03.09.79)

(31) Priority Application Number: 35616/78

(32) Priority Date: 5 September 1978 (05.09.78)

(33) Priority Country: GB

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(81) Designated States: BR, DE (European patent), DK, FR (European patent), GB (European patent), JP, NL (European patent), SE (European patent), US.

Published
With international search report

(54) Title: PREVENTING FOULING ON MARINE STRUCTURES

(57) Abstract

Fouling of a marine structure, such as an oil production platform or a drilling rig, by seaweed, barnacles, mussels and the like, is prevented by securing to the underwater surface of the marine structure a coated flexible sheet material, the outermost surface of which is a layer of silicone rubber. The preferred coated flexible sheet material, useful as an anti-fouling cladding, is a coated fabric having an outermost coated surface which is a layer of silicone rubber/silicone oil mixture produced by curing a room-temperature-vulcanisable silicone rubber having hydroxyl end groups in the presence of a silicone oil.

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Preventing fouling on marine structures

This invention relates to the prevention of fouling on marine structures, (namely man-made structures, frequently of metal but also of other structural materials such as concrete, which are at least partially immersed in sea-water during normal use, either as static structures or as moving objects), for example oil production platforms and drilling rigs. Such structures are liable to heavy fouling from seaweed, barnacles, mussels and the like. The resistance of a thick layer of fouling to waves and currents can cause unpredictable and potentially dangerous stresses in the marine structure particularly when this is resting on the sea bed in deep water.

The use of anti-fouling paints containing biocides which are gradually released from the paint does not provide a permanent solution to fouling of static marine structures. These anti-fouling paints have a limited active life and re-painting an oil platform in situ is impractical.

Moreover, marine structures such as oil production platforms have to be inspected periodically for corrosion and for stress cracks in the structure. The structure needs to be free from fouling for proper inspection.

A method according to the invention for preventing fouling of a marine structure comprises securing to an underwater surface of the marine structure (i.e. a surface which in normal use of the marine structure is at or below the water level) a coated flexible sheet material, the outermost (i.e. water-contacting) surface of which is a layer of silicone rubber.

The invention also includes a marine structure having secured thereto at and/or below the water-line a coated flexible sheet material, the outermost surface of which is a layer of silicone rubber.

Silicone rubbers have been proposed for use in anti-fouling paints or films in British Patent Specifications Nos. 1,307,001 and 1,470,465. Their anti-fouling action is unique in that they do not poison marine organisms but prevent them securing satisfactory adhesion to the surface, apparently by a physical effect. There are, however, pract-

ical difficulties in the use of silicone rubber anti-fouling paints or films. It is difficult to make them adhere well to a marine surface and the applied paint films or coatings are mechanically rather weak and liable to damage. The present invention employs a reinforcing sheet coated with a silicone rubber layer and this gives mechanical support to the silicone rubber and the fabric can be securely attached to the marine structure.

The sheet material used as substrate for the silicone rubber layer should be a reinforcing sheet material, i.e. a sheet of it should have substantially greater tensile and tear strength than a silicone rubber sheet of equal weight. Preferably it is a fabric, for example a plain woven fabric of nylon or polyester yarn. Alternatively, however, it can be a tough plastics film such as an oriented polyester or polypropylene film.

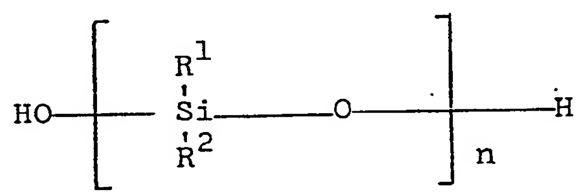
The silicone rubber can be a cured room-temperature-vulcanisable silicone rubber or a heat-cured (i.e. cured heat-curable) silicone rubber. We have found that the best anti-fouling performance is obtained using a cured room-temperature-vulcanisable silicone rubber but the heat-cured silicone rubbers are also effective and can be readily applied by coating techniques such as dip coating.

When a fabric is used as the substrate, more than one coating layer is usually applied to the fabric to build up sufficient thickness of coating to obscure the weave of the fabric. Only the outermost coating need be of silicone rubber and from cost considerations it is generally preferred that at least one inner layer is an alternative elastomer such as natural rubber, nitrile rubber, neoprene polychloroprene rubber or Hypalon rubber which is based on polyethylene substituted by chlorine and sulphonyl chloride groups. The first coat applied to the fabric may be a keying coat, for example a rubber solution containing a polyfunctional isocyanate, and an adhesion promoter can also be applied, for example by dip coating with a solution containing a resorcinol resin and/or an epoxy resin, as is known in fabric coating. Good adhesion of the silicone rubber to the inner elastomer coating(s) can be achieved by the use of one

or more intermediate layers based on a mixture of the silicone rubber and the elastomer used for the inner layer(s).

The thickness of the silicone rubber coating should be sufficient to give a continuous surface of silicone rubber. The thickness is usually equivalent to a coating weight of at least 10 g/m^2 and preferably about 25 g/m^2 and can be up to 1 mm or even more.

The room-temperature-vulcanisable silicone rubber is preferably an oligomeric silicone rubber having hydroxyl end groups, for example those sold under the trade marks Silocoset 105, Dow Corning RTV 3110 and General Electric RTV 11. Such a silicone rubber generally has a molecular weight in the range 40,000-100,000 and a viscosity of 10-1,000 Stokes before curing and can be represented by the formula



where n is an integer corresponding to the degree of polymerisation and R^1 and R^2 are the same or different alkyl, aryl or vinyl groups, the repeating units being identical or different. The silicone subber is generally cured using an aminoacetoxyoxime or alkoxysilane crosslinking agent and a curing catalyst, for example dibutyl tin dilaurate, stannous octoate or a platinum salt.

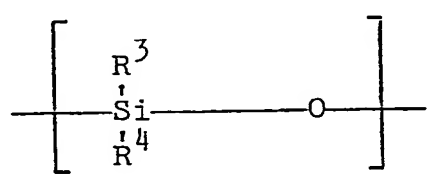
The heat-curable silicone rubber is generally based on a long-chain siloxane, for example a polydimethyl siloxane which can be crosslinked by heat in the presence of a tin-containing catalyst or one which can be crosslinked using an oxidising agent, for example by the incorporation of a peroxide curing agent.

The room-temperature-vulcanisable silicone rubber can be subjected to an accelerated cure at temperatures above ambient, for example in the range 50°-100°C. An intermediate layer of a heat-curable silicone rubber can be used to improve the adhesion of the room-temperature-vulcanisable silicone rubber, optionally with a further layer which is a

mixture of the heat-curable silicone rubber and the room-temperature-vulcanisable silicone rubber. The preferred curing procedure for such a multi-coated sheet is to heat-cure, usually at a temperature in the range 100-200°C, when all the layers containing heat-curable material have been applied and to cure a subsequently applied layer or layers of room-temperature-vulcanisable silicone rubber at a temperature which is in any case substantially below that used for heat-curing and may be as low as ambient temperature.

The room-temperature-vulcanisable silicone rubbers are slow in curing compared to many fabric coatings. It may be preferred to interleave the final coated sheet material with a sheet having a release surface of, for example, polyethylene, so that the coated sheet can be rolled up before the silicone rubber is fully cured.

The silicone rubber preferably contains a silicone oil, for example as described and claimed in our British Patent Specification No. 1,470,465. The silicone oil is generally a polymer of molecular weight 2,000-30,000 and viscosity 20-1,000 centistokes and comprises repeating



units where R^3 and R^4 are the same or different alkyl or aryl groups, the repeating units being identical or different. Particularly preferred silicone oils are those where R^3 is an alkyl group and R^4 is an aryl group in at least some of the repeating units, for example methylphenyl silicone oils such as those sold under the trade marks Dow Corning DC 510, DC 550 and DC 710. Silicone oils containing fluorocarbon groups can also be used. The silicone oil is generally used in a proportion of 1-50 <u>per cent</u> by weight, preferably 5-30 <u>per cent</u> by weight, based on the silicone rubber.

A preferred material according to the invention for use as an anti-fouling cladding for a marine structure therefore

comprises a coated flexible substrate, preferably a coated fabric, optionally one or more coated inner layers of an elastomer, and an outermost coated layer of a cured silicone rubber, preferably a layer of a silicone rubber/ silicone oil mixture produced by curing a heat curable silicone rubber or more preferably a room-temperature-vulcanisable silicone rubber having hydroxyl end groups in the presence of 1-50 per cent by weight of the silicone oil. When a silicone oil is used it is generally mixed with the silicone rubber before curing, so that the silicone rubber is cured in the presence of the silicone oil to give good dispersion of the oil on the rubber.

The coated flexible sheet material, e.g. fabric, is preferably secured to the marine structure by wrapping it around an underwater surface of the marine structure and securing it by clamping bands. This method of securing allows relatively easy removal of the cladding for inspection of the structure. The coated flexible sheet material can be in the form of a band which is spirally wrapped around the structure, or for larger diameter structures a sheet of the coated flexible sheet material can be secured around the structure by clamping bands. This procedure, unlike painting, can be carried out under water.

In an alternative method of securing the coated flexible sheet material to the marine structure, the reverse face of the flexible sheet material is coated with an adhesive capable of bonding it to an underwater surface of the marine structure. The particular adhesive depends on the conditions under which the anti-fouling cladding is to be bonded to the marine structure. Where the cladding is to be applied to the structure before it is immersed in the sea any sea-water-resistant adhesive can be used, for example a nitrile or neoprene rubber or an epoxy adhesive. Where the cladding is to be applied to a structure *in situ*, for examle at and/or below the water line of an oil production platform already in position on the sea-bed, the adhesive must be capable of forming a bond under water. One example of an underwater adhesive is an epoxy resin, for example a low

molecular weight condensate of bisphenol-A epichlorhydrin, used in conjunction with a polyamine curing agent which is insoluble in and insensitive to water.

When adhesives are not used, the reverse face of the flexible sheet material can be left uncoated, or a protective rubber coating can be applied.

Although the invention is particularly applicable to the prevention of fouling of marine structures which are static for long periods such as oil production platforms, drilling rigs and fish farming tanks, the coated flexible sheet material can also be applied to ships' hulls, for example by adhering sheets of the coated flexible sheet material to the ship's hull. The coated flexible sheet material is preferably applied to the marine structure from the highest point the sea reaches on the structure to a depth of up to 10 metres below the lowest water line.

The invention is illustrated by the following examples:

Example 1

A plain weave fabric of 165 cm width formed from 940 decitex low shrinkage nylon yarn was dipped in a solution of resorcinol/formaldehyde resin, coated with a key coat of a rubber solution containing a polyfunctional isocyanate and then successive coats of neoprene rubber to a total coating weight of 250 grams per square metre. This obscured the fabric weave. The back face of the fabric was coated similarly to a total coating weight of 50 grams per square metre. The fabric was coated with a 25 grams per square metre coat of a mixture of nitrile rubber and silicone rubber in a weight ratio of 2:1 followed by a coat of a mixture of these two rubbers in a weight ratio of 1:2. The silicone rubber used was in each case a heat-curable elastomer based on a polydimethyl siloxane sold by Dow Corning as "FC.227". The product was then coated with a 50 grams per square metre coat of a composition of the same silicone rubber containing 5 per cent by weight of a fluorinated methyl phenyl silicone oil. The coated fabric was finally cured at 160°C for 3 minutes.

The silicone rubber/silicone oil surface of the coated

fabric, when immersed in sea water off the south coast of England, remained free from fouling for a period of six months, and had a much reduced rate of fouling thereafter compared to an uncoated surface. It can be applied to a marine structure by cutting lengthways into two or more bands which can be spirally wrapped around the marine structure and then secured by clamping bands or the coated fabric can be wrapped at full width around a large marine structure such as the leg of an oil production platform and secured by clamping bands.

Example 2

A neoprene rubber-coated fabric as described in Example 1 was coated with a 25 g/m^2 coat of 1:1 by weight mixture of neoprene rubber and "FC227" heat-curable silicone rubber followed by a 25 g/m^2 coat of silicone rubber alone, then a 25 g/m^2 coat of 1:1 by weight mixture of the "FC227" silicone rubber with Dow Corning RTV 3110 room-temperature-vulcanisable silicone rubber. The coated fabric was then heat cured for 5 minutes at 140°C.

The coated fabric was further coated with a 25 g/m^2 coat of the RTV 3110 silicone rubber which was allowed to cure at ambient temperature and finally with a 25 g/m^2 coat of a composition of the RTV 3110 silicone rubber containing 20 per cent by weight of a methyl phenyl silicone oil sold by Dow Corning under the trade mark "DC550". This was allowed to cure at ambient temperature and the fabric was then attached to a raft and immersed in sea water off the south coast of England. It has remained free from fouling for a period of six months. Panels having a similar surface of a cured room-temperature-vulcanisable silicone rubber compound with silicone oil have resisted fouling for up to five years.

The fabric can be applied and secured to a marine structure as described in Example 1.

CLAIMS

1. A method of preventing fouling of a marine structure characterised by securing to the underwater surface of the marine structure a coated flexible sheet material, the outermost surface of which is a layer of silicone rubber.

2. A method according to claim 1 characterised in that the silicone rubber is a cured room-temperature-vulcanisable silicone rubber.

3. A method according to claim 1 characterised in that the silicone rubber is a heat-cured silicone rubber.

4. A method according to any of claims 1 to 3 characterised in that the silicone rubber is mixed with a silicone oil.

5. A method according to any of claims 1 to 3 characterised in that the coated sheet material is a fabric which is coated with at least one inner layer of an elastomer (other than silicone rubber) selected from natural rubber, neoprene rubber or chlorinated polyethylene rubber as well as an outermost layer of silicone rubber.

6. A method according to any of claims 1 to 3 characterised in that the thickness of the silicone rubber layer is from a thickness equivalent to a coating weight of 10 grams per square metre up to a thickness of one millimetre.

7. An anti-fouling cladding for a marine structure composed of a coated flexible sheet material comprising a flexible substrate, optionally one or more inner coated layers of an elastomer and an outermost coated layer of a cured silicone rubber.

8. An anti-fouling cladding for a marine structure comprising a coated fabric, the outermost coated surface of which is a layer of a silicone rubber/silicone oil mixture produced by curing a room-temperature-vulcanisable silicone rubber having hydroxyl end groups in the presence of 1 to 50 per cent by weight of the silicone oil.

9. An anti-fouling cladding according to claim 8 characterised in that the silicone oil is a methyl phenyl silicone oil.

10. A marine structure having a reduced liability to fouling, characterised in that it has secured thereto at and/or below the waterline a coated flexible sheet material the outermost surface of which is a layer of silicone rubber.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 79/00146

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

B 63 B 59/00; B 08 B 17/00; C 09 D 5/16; C 08 L 83/00

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int.Cl.	C 09 D 5/16; B 63 B 59/00; B 08 B 17/00; B 08 B 17/02; B 08 17/04

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3702778, published November 4, 1972, see claims 1 to 3; column 4, lines 34 to 40; the examples 1,2,3 and 5, W.J. Mueller --	1,2,3,10
X	GB, A, 1175978, published January 1, 1970, see claim 1, page 2, lines 98-120, Goodrich --	1,2,3,5, 7,10
	FR, A, 2297901, published August 13, 1976, see claims 1 and 2, The International Paint Company Ltd. --	1,2,3,4,8,9, 10
	DE, A, 2101074, published July 22,1971, see claims 1 to 5, Kroeyer K.K.K. ----	1,2,3

* Special categories of cited documents: [15]

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
23rd November 1979	4th December 1979
International Searching Authority [1]	**Signature of Authorized Officer** [20]
European Patent Office	G.L.M.KRUYDENBERG

Form PCT/ISA/210 (second sheet) (October 1977)